Inorganic-organic hybrid material formed between silica sol-gel and polyaniline.

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Introduction

There is an increasing interest in inorganic-organic hybrids as electrodes and solid electrolytes. We are studying hybrids formed by a combination of a conducting polymer with a sol-gel matrix. Nanostructured materials are obtained with novel complementary physico-chemical properties. The resulting materials have electrical and optical properties inherent to the polymers but have better mechanical, thermal and chemical resistance than the polymer alone. Electroactive polymers (e.g. polyaniline and polypyrrole) were inserted into porous silica sol-gels by a template synthesis (1, 2). The pores of the inorganic solid serve as template that determines the size of the synthesized product.

We are exploring the idea of controlling the process of aniline polymerization by varying the pore size of the silica. The resulting inorganic-organic hybrid may be used as thin films (i.e. as conventional modified electrodes) or in a form of bulk solid or semi-rigid systems of the gelling matrix (i.e. by solid-state voltammetry in the absence of contact with liquid electrolyte phase).

The size of the gel pores was controlled in different ways: 1) in the case of silica gel monoliths, by applying a different time of aging and 2) in the case of silica gel thin films, by using a different pHs of the sol and/or by adding surfactants (e.g. PAMAM dendrimers or Triton X114).

Experimental:

Electropolymerization of aniline inside of bulk monolith of silica sol-gel. The silica was made with tetramethyl orthosilicate (TMOS) as the precursor. Sols were prepared by mixing TMOS, methanol, 0.1M HCl, 0.2M KCl, and aniline. A solid - state cell was constructed using a Tygon mold fitted onto glassy carbon, which serves as the counter electrode, Ag wire, which was electroplated with AgCl, was the reference electrode, and glassy carbon was the working electrode. The sol was pipetted into the mold. The sol - loaded assembly was put into humidity chamber and allowed to dry for 1, 3 or 5 days. After that period the working electrode was inserted into the gelling matrix. The polymerization of aniline was done in the potentiodynamic mode.

Electropolymerization of aniline on silica modified ITO electrode. Stock sols were prepared by mixing: tetraethyl orthosilicate (TEOS) with HCl (0.01M, or 0.1M or 1M) and deionized water. In some cases, surfactant was added (Triton X114 or PAMAM G0 or G4). The sol was stirred at room temperature for 2 h, diluted with methanol and spin-coated at 2000 rpm on the ITO glass plate.

The formation of PANI on TEOS derived sol-gel films was carried out electrochemically by potentiodynamic mode.

Results and Discussion:

The hypothesis is that any variation of the sol-gel processing that decreases the pore size of the silica will lead to formation of dimers and oligomers rather than polyaniline. Factors known to decrease pore size of sol-gel materials are increasing aging time and increasing pH. In addition, the inclusion of surfactants in the sol increases the pore size. The first experiments used the solid state cell. The data supported our hypothesis. Cyclic voltammetry of polyaniline generally showed three redox processes. Specifically the redox process at about 0.5V is known to be due short chain units imbedded into polymer matrix, while those at 0.2V and 0.8V are from the polymer. The ratio of peak currents at 0.2V and 0.5 on i/E curve is indicative of the ratio of polymer/oligomer. After I day of aging the oxidation of aniline resulted in formation of polyaniline; three redox peaks are observed on voltammogram. However, aniline oxidation after aging the gels for 3 and 5 days resulted primarily in the formation of short chain units (dimers or oligomers). In the latter case only one redox peak is observed at 0.5V.

The second set of experiments was performed on ITO -coated electrode. The results followed the trends from the solid-state cell. Of particular importance was that a role of hydrogen ions entrapped in the sol-gel matrix covering the ITO electrode, in the catalysis of the polymerization of aniline. The results suggested by cyclic voltammetry will be tested by independent methods, spectroelectrochemistry and mass spectrometry.

References:

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